Correlated Electron Compounds: from real materials to model systems and back again

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Stereotypical theoretical physicist’s view of condensed matter physics

Crystal structure $\Rightarrow$ Quantum Field Theory

$\Rightarrow \frac{\kappa}{2} \epsilon^{\mu \nu \lambda} A_\mu \partial_\nu A_\lambda + ...$

These lectures--where we are on attempts to do better, connecting material-specificity to behavior.

Periodic table from J H Wood; quoted in Z Fisk 2010 KITP talk

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YBa$_2$Cu$_3$O$_7$
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Image from www.tkk.fi/
YBa$_2$Cu$_3$O$_7$

Image from www.tkk.fi/

Wu et. al. PRL 58 908 (1987)
YBa$_2$Cu$_3$O$_7$

Image from www.tkk.fi/

??What is special about this material??
‘Oxide Superlattices’

Ohtomo, Muller, Grazul and Hwang, Nature 419 p. 378 (2002)

\[(\text{LaSrO}_3)_m(\text{LaTiO}_3)_n\]

\text{SrTiO}_3:\quad d^0 \text{ “band” insulator}

\text{LaTiO}_3:\quad d^1 \text{ “Mott” insulator}

‘any’ desired \((n,m)\) can be synthesized
Many systems now being made: many effects can be produced

Luders et al

‘Room temperature magnetism in LaVO$_3$/SrVO$_3$ superlattices--but not in bulk alloy

??Why room T magnetism in superlattice??
Chaloupka/Khaliullin: ?superlattices allow us to design a new high-$T_c$ superconductor?

Idea:

Bulk LaNiO$_3$ Ni [d]$^7$
(1 electron in two degenerate e$_g$ bands).

In correctly chosen structure, split e$_g$ bands, get 1 electron in 1 band--”like” high-Tc
Chaloupka and Khalliulin argue

(1) Pseudocubic LaNiO$_3$

Relevant orbitals: $e_g$ symmetry
Ni-O antibonding combinations

$3z^2-r^2$
Hybridizes strongly along $z$
Hybridizes weakly in $x$-$y$

$x^2-y^2$
Hybridizes strongly along $x$-$y$
Hybridizes very weakly in $z$

2 orbitals transform as doublet in cubic symmetry

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Heterostructuring breaks the symmetry
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$3z^2-r^2$ orbital goes up in energy
Heterostructuring breaks the symmetry

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Result: planar array of $x^2-y^2$ orbitals
‘just like CuO$_2$ high Tc superconductors’
Heterostructuring breaks the symmetry

\[ 3z^2-r^2 \text{ orbital goes up in energy} \]

Result: planar array of \( x^2-y^2 \) orbitals
‘just like CuO\(_2\) high Tc superconductors’

Query: How do we know if this is right?
More generally:

If experimentalists can make ‘anything’ --what would one want to make?

How do we connect crystal structure/atomic properties to interesting electronic behavior?
Why is it hard?
Why is it hard?

We know the Hamiltonian
Why is it hard?

We know the Hamiltonian

\[ H = \sum_i -\frac{\nabla^2}{2m_e} + \sum_i V_{ext}(r_i) + \frac{1}{2} \sum_{i \neq j} \frac{e^2}{|r_i - r_j|} \]
Why is it hard?

We know the Hamiltonian

$$\mathbf{H} = \sum_i \frac{-\nabla_i^2}{2m_e} + \sum_i V_{ext}(r_i) + \frac{1}{2} \sum_{i \neq j} \frac{e^2}{|r_i - r_j|}$$

We know the equation
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We know the equation

\[ H\Psi_n = -i\partial_t \Psi_n \]
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So stop complaining and solve it (?!)

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Not so fast:
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Typical lattice constant: 4 Angstrom
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Interesting length \(\sim 100\) Angstrom
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Interesting length ~100 Angstrom

=> ~1000 electrons with 3 \((x,y,z)\) coordinates.

Interaction ‘entangles’ coordinates=>
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\[ \Psi(\vec{r}_1, \ldots, \vec{r}_{1000} \ldots) \]
Not so fast:

Typical lattice constant: 4 Angstrom

Interesting length \( \sim 100 \) Angstrom

\( \Rightarrow \sim 1000 \) electrons with 3 (x,y,z) coordinates. Interaction ‘entangles’ coordinates=>

\[ \psi(\vec{r}_1, \ldots \vec{r}_{1000} \ldots) \] Intractable
Not so fast:

Typical lattice constant: 4 Angstrom

Interesting length ~100 Angstrom

=> ~1000 electrons with 3 (x,y,z) coordinates.

Interaction ‘entangles’ coordinates =>

\[ \Psi(\vec{r}_1, \ldots \vec{r}_{1000} \ldots) \]

Schroedinger equation for \[ \Psi \]

Intractable

Even worse: \[ \Psi \] is fully antisymmetric function of spins and coordinates
Sign problem:

*electrons are fermions: wave function is antisymmetric

\[ \psi(r_1, \sigma_1; r_2, \sigma_2; \ldots) = -\psi(r_2, \sigma_2; r_1, \sigma_1; \ldots) \]

but always exists (much) lower energy (physically inadmissible) symmetric wave function \( \Rightarrow \) straightforward numerics suffers from ‘sign problem’
Need some other approach!
Work-horse of materials theory: density functional theory

Key idea: don’t solve problem directly. Use solution of auxiliary problem to obtain (limited class of) information about problem of interest
Density Functional theory I

Phys. Rev. 136, B864 (1964)

Basic Theorem (Hohenberg and Kohn): ∃ functional $\Phi$ of electron density $n(r)$: minimized at physical density; value at minimum gives ground state energy

$$\Phi\{n(r)\} = \Phi_{univ}\{n(r)\} + \int (dr)V_{lattice}(r)n(r)$$

$\Phi_{univ}$ is universal: only material dependence is in $2^{nd}$ term
Sketch of Proof

\[ H = \sum_i \frac{-\nabla_i^2}{2m_e} + \sum_i V_{ext}(r_i) + \frac{1}{2} \sum_{i \neq j} \frac{e^2}{|r_i - r_j|} \]

(1) Ground state energy \( E \) is functional of \( V_{ext} \)

solution of \( H \Psi = (H_0 + V_{ext}) \Psi = E \Psi \)
gives mapping \( V_{ext} \rightarrow E \)

Note \( E = \langle \Psi | H_0 | \Psi \rangle + \int d^3r V_{ext}(r)n(r) \)

(2) Ground state density \( n(r) \) is functional of \( V_{ext} \)

\( \Psi \) from solution of \( H \Psi = E \Psi \rightarrow n(r) \)
Key statement

**V_{ext} is unique functional of density n(r) (up to constant)**

Suppose not.

Then 2 potentials, $V_1 \neq V_2 + const \rightarrow n(r)$

→ 2 Hamiltonians, $H_{1,2}$, energies $E_{1,2}$ and $\Psi_{1,2}$

Thus $E_1 = <\Psi_1 | H_1 | \Psi_1 > < < \Psi_2 | H_1 | \Psi_2 >$

But $H_1 = H_2 + V_1 - V_2$

So $E_1 < E_2 + \int d^3 r n(r) (V_1(r) - V_2(r))$
Thus

\[ E_1 < E_2 + \int d^3r n(r) (V_1(r) - V_2(r)) \]

\[ E_2 < E_1 + \int d^3r n(r) (V_2(r) - V_1(r)) \]

Add. Get

\[ E_1 + E_2 < E_2 + E_1 \]

!!contradiction!!

Thus mapping \( n(r) \rightarrow V_{\text{ext}}(r) \rightarrow E \)

Ground state energy is unique functional of density. Can go on to show that functional is minimal at density corresponding to given \( V_{\text{ext}} \)
So to get energy

1. Put $V_{\text{ext}}(r)$ into universal functional
2. Minimize

Unfortunately

- Don't know universal functional
- Don't know how to perform minimization
To minimize functional: solve auxiliary single-particle problem + self-consistency condition

\[
\left( -\frac{\hbar^2}{2m} \nabla^2 + V_{\text{ions}}(r) + V_{\text{hartree}}(r) \right) \psi_n(r) \\
+ V_{\text{XC}}(\{n(r)\}) \ast \psi_n = E_n \psi_n(r)
\]

V_{\text{XC}}: exchange correlation potential’ (possibly non-local) determined by electron density. Not known.

Wave function (in principle) no meaning except

Self-consistency:

\[
n(r) = \sum_{E_n < \mu} \psi_n(r) \ast \psi_n(r)
\]
DFT 2

(2) Uncontrolled (but apparently decent) approximation (recipe) for $V_{\text{ext}}[\{n(r)\}]$.

--‘Local density approximation’
for uniform electron gas $n(r)\rightarrow n$.
numerics gives $V_{\text{el-gas}}(n)$.
Replace $V_{\text{ext}}[\{n(r)\}]$ by $V_{\text{el-gas}}(n=n(r))$

--Host of other approximations (GGA, B3LYP, ...) (all uncontrolled; tested by comparison to experiment...)
Result: procedure that works for many purposes.
Essential computational task: solve 1 particle schroedinger eq in some $V(n(r))$; self-consist
Density functional band theory

Believed good for:

• Total energies
• Crystal structures
• Phonon Frequencies (restoring force=electron energy)
• Identification of relevant electronic orbital

Not so good for:

• Dynamics
• Thermodynamics
• Phase transitions
• Local moment/Mott physics
Density Functional Theory: Issues

$$\Phi[\{n(r)\}] = \Phi_{univ}[\{n(r)\}] + \int (dr)V_{lattice}(r)n(r)$$

Density is not the optimal variable: phases with quite different physical properties have almost the same density.
Density Functional Theory: Issues

Ground state is not the only interest: different phases at different temperatures: need theory with local moments, entropic effects

\[ \chi \sim \frac{1}{T} \]

Local magnetic moment?
Density Functional Theory: Issues

Ground state is not the only interest: excitation spectrum also important

Photoemission (electron removal spectrum)

dots: data
lines: band theory

Shakeoff (side) band present in data, absent in band theory

Summary: density functional theory

• Quantities of interest obtained from solution of auxiliary problem + self consistency condition
• Uncontrolled but in practice very useful approximation
• Built to get ground state density, energy => difficulties with excitation spectrum, higher T behavior, phase transitions to other ground states
To deal with excitation spectrum: fermi liquid theory
Consider `free’ (no potential) fermions interacting via short ranged interaction (physical example: \( ^3\text{He} \))

Neglect interactions: \( H = - \sum_i \frac{\nabla_i^2}{2m} \)

Solution: antisymmetrized product (‘Slater Determinant’) of plane waves

\[
\text{Det} \left[ e^{i\vec{k}_j \cdot \vec{r}_i} \right]
\]
Physical Content

Ground state: ‘filled fermi sea’

2 dimensional picture of region of $k$ space with occupied states in green

Excited states: particle-hole pairs

Label wave function by excitations above ground state
Physical content II

Noninteracting fermions

Excited states: particle-hole pairs

- Particle (or hole) energy $\sim$ distance from fermi surface:
  $$E = v_F ||k| - k_F|$$
- Susceptibilities, specific heat coefficient constant (at low T) and proportional to particle mass $m$
Physical content: III

Noninteracting case: each particle and hole propagates freely.
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Interacting case:

(1) Energy of excited particle depends on how many other particles/holes are excited
Physical content: III

Noninteracting case: each particle and hole propagates freely.

Interacting case:

1. Energy of excited particle depends on how many other particles/holes are excited
2. M particle/M hole state not exact eigenstate: particle can e.g. decay into particle +(p-h pair)
Physical content: III

Noninteracting case: each particle and hole propagates freely.

Interacting case:

(1) Energy of excited particle depends on how many other particles/holes are excited
(2) M particle/M hole state not exact eigenstate: particle can e.g. decay into particle + (p-h pair)
As particle approaches fermi surface, phase space for decay decreases
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Hide other particles, so can focus on decay of 1 particle.
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Energetics of decay:

Hide other particles, so can focus on decay of 1 particle
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Energetics of decay:

Initial state: energy $E_{\text{initial}}$

Hide other particles, so can focus on decay of 1 particle.
As particle approaches fermi surface, phase space for decay decreases

Energetics of decay:

Initial state: energy \( E_{\text{initial}} \)

Final state: energy \( E_f + E_p + E_H \)

Hide other particles, so can focus on decay of 1 particle
As particle approaches fermi surface, phase space for decay decreases

Energetics of decay:

Initial state: energy $E_{\text{initial}}$

Final state: energy $E_f + E_p + E_H$

$= E_{\text{initial}}$

$\Rightarrow$ all 3 final states must be closer to fermi surface than initial state $\Rightarrow$ decay prob $\sim E^2$
Low energy excitations:

1. Decay process $p \rightarrow p + (p, h)$ is negligible
2. Modification of energetics due to other excitations not negligible

I gave a pictorial sketch of a perturbative argument for (1) and I ask you to believe (2).

Landau, then Luttinger, Ward, Nozieres, and others provided an increasingly sophisticated set of formal arguments justifying these statements and exploring their consequences.

Result: ‘Fermi Liquid Theory’
Fermi Liquid Theory References

Books

Abrikosov, Gorkov and Dzyaloshinksi, *Methods of Quantum Field Theory in Statistical Physics*

Pines and Nozieres: *Theory of Quantum Liquids*

Nozieres: *Interacting Fermi Systems*

Renormalization Group Point of View

Result:

In many circumstances, low energy properties of interacting fermi systems are those of noninteracting systems, but with renormalized parameters.
Formalism: electron Green function

Define: **Exact eigenstates** \( |\Psi^m_{N+1}(k) > \)

of N+1 particle system

**momentum** \( k \), **energy** \( E^m_k \)

relative to \( N \)-particle ground state \( |GS > \)

Define: **electron Green function** \( G(k, \omega) \)

\[
= \int dt e^{-i\omega t} \mathcal{T} \left< GS \left| \{ \psi_k(t), \psi^\dagger_k(0) \} \right| GS \right>
\]

\( \psi^\dagger_k \) creates electron in state with wave function \( \sim e^{i\vec{k} \cdot \vec{r}} \)

\( \mathcal{T} \) is time ordering symbol
Spectral representation

\[ G^R(k, \omega) = \int \frac{dx}{\pi} \frac{A(k, x)}{\omega - x - i\delta} \]

Spectral function

\[ A(k, \omega) = Im \left[ G^R(k, \omega) \right] \]

\[ = \sum_m < GS|\psi_k|\Psi_{N+1}^m > < \Psi_{N+1}^m|\psi_k^\dagger|GS > \delta(\omega - E_{N+1}^m) \]

\[ + \sum_m < GS|\psi_k^\dagger|\Psi_{N-1}^m > < \Psi_{N-1}^m|\psi_k|GS > \delta(\omega - E_{N-1}^m) \]

Measures overlap of exact eigenstates with ‘single-particle state created by \( \psi_k^\dagger \)
Spectral representation II

Noninteracting system: $\psi_k^\dagger$ creates an exact eigenstate, say $m = m_1$

$$\psi_k^\dagger |GS > = |\Psi_{N+1}^m(k) > \delta_{m,m_1}$$

Spectral function is a delta function

$$A(k, \omega) = \delta(\omega - E_k)$$
Spectral representation III

General interacting system: state created by $\psi_k^\dagger$ does not closely resemble any eigenstate; has overlap with all $\langle \Psi_{N+1}^m(k) | \psi_k^\dagger | GS \rangle = f(m)$

Spectral function is a smooth function
Fermi liquid: as $k \to k_F$, the state created by $\psi_k^\dagger$ tends to have some overlap with one unique state, as well as with a continuum of others

$$<\Psi_{N+1}^m(k)|\psi_k^\dagger|GS> = Z_k \delta_{m,m_1} + f(m)$$

Spectral function tends to a delta function (quasiparticle peak) plus smooth (‘incoherent part’) background

Important concept: quasiparticle weight $Z_k$
Angle-Resolved Photoemission (ARPES) measures (occupied state part of)

\[ A \ (\text{up to matrix element}) \]

Noninteracting Fermi liquid

\[ Z: \text{relative weight of near fermi surface peak} \]

\[ v^*: \text{peak dispersion} \]

\[ \text{Im } \Sigma: \text{peak width} \]

Fig. 3, Damascelli, Hussain and Shen RMP 75 473 (2003)
Spectral representation V

Alternative mathematical formulation: self energy

\[ G(k, \omega) = \frac{1}{\omega - \varepsilon_k - \Sigma(k, \omega)} \]

Self energy \( \Sigma(k, \omega) \) expresses difference between actual electron propagation and electron propagation in reference noninteracting system with dispersion \( \varepsilon_k \)
Spectral representation V

Self energy has real and imaginary parts.

\[ A(k, \omega) = \frac{\text{Im} \Sigma(k, \omega)}{\left( \omega - \varepsilon_k - \text{Re} \Sigma(k, \omega) \right)^2 + \text{Im} \Sigma(k, \omega)^2} \]

Real part expresses renormalization of dispersion, overlap with exact eigenstate.
Imaginary part expresses quasiparticle lifetime

Fermi liquid: \[ \text{Im} \Sigma(k, \omega \to 0) \to 0 \]

\[ v_F^* = Z \left( \partial_k \varepsilon_k + \partial_k \text{Re} \Sigma(k, \omega) \right)_{k=k_F} \]

\[ Z = \left( 1 - \frac{\partial \text{Re} \Sigma(k_F, \omega)}{\partial \omega} \bigg|_{\omega \to 0} \right)^{-1} \]
Fermi liquid theory

Arrangement of many-body physics formalism to focus on coherent part of $G$, with effect of incoherent parts being subsumed in renormalizations, interaction vertices etc.
Different perspective on spectral function, fermi liquid theory

Anderson impurity model

\[ H_{AIM} = \sum_{\sigma} \varepsilon_0 d_{\sigma}^\dagger d_{\sigma} + Un_{\uparrow}n_{\downarrow} \]

\[ + \sum_{k\sigma} \left(V_k c_{k\sigma}^\dagger d_{\sigma} + H.c.\right) + \sum_{k\sigma} \varepsilon_k c_{k\sigma}^\dagger c_{k\sigma}. \]

1 orbital (d), subject to interaction (U) and coupled to non-interacting continuum (c)

Not trivial because V-term does not commute with U term

0-dim model. Perturbation in U converges at all U
U=0: solvable hybridization problem:

Physics: scattering resonance in continuum. Describe by Green function for d-electrons

\[ G_d(\omega) = \frac{1}{\omega - \varepsilon_d - \Delta(\omega)} \]

key parameter: hybridization function

\[ \Delta(\omega) = \sum_k V_k^2 \left( \mathcal{P} \frac{1}{\omega - \varepsilon_k} + i\pi \delta(\omega - \varepsilon_k) \right) \]

real part: level shift due to coupling to continuum
imaginary part: decay of electron from localized orbital to continuum
U=0: solvable hybridization problem:

**Physics:** scattering resonance in continuum. Describe by Green function for d-electrons

\[ G_d(\omega) = \frac{1}{\omega - \varepsilon_d - \Delta(\omega)} \]

**key parameter:** hybridization function

Fill resonance up to chemical potential
‘Friedel sum rule’

\[ n_d = \text{ArcTan} \left[ \frac{\text{Im} \ G_d^{-1}(\omega = \mu)}{\text{Re} \ G_d^{-1}(\omega = \mu)} \right] \]
V=0: isolated ‘atom’

Impurity occupation number $n_d$: conserved

If $\varepsilon_d < \mu$

1 electron  2 electrons

$\text{Im}G_d(\omega)$

$\varepsilon_d \quad \mu \quad 2\varepsilon_d + U$

Note: 2 1-electron states: up, down
turn on V

impurity occupation number $n_d$: not conserved

Guess: states broaden

If $\varepsilon_d < \mu$

1 electron

2 electrons

$\text{Im} G_d(\omega)$

$\varepsilon_d$ $\mu$ $2\varepsilon_d + U$
But recall Friedel sum rule

0-d system, no phase transition as function of U, so ratio of Im to Re G at chemical potential has to be consistent with density.

Result: 3 peak structure with ‘Kondo resonance’ in center

Wang, Spataru, Hybertsen, AJM PRB77 045119 (at largest U, T in calculation not low enough)
Low energy physics

Renormalized scattering resonance

‘Local fermi liquid theory’. Weight of central peak $\leftrightarrow Z$
How would density functional theory represent this solution?

Only choice: one single scattering resonance, with properties tuned to reproduce energy.
We will see:

Anderson impurity model is an auxiliary problem whose solution gives insight into many-body electronic structure.